THE STRUCTURE OF THE ADDUCT OF CINNAMALANILINE AND DIMETHYLACETYLENEDICARBOXYLATE

BY

HERMAN JULIAN SAMPSON, JR.

A.B., Augustana College, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1946

URBANA, ILLINOIS

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INTRODUCTION

Diels and Alder (1,2,3) observed that dimethylacetylenedicarboxylate added in an abnormal manner to compounds in which nitrogen was present in a cyclic diene system. This was found to be true for imidazoles, pyridines, quinolines, and isoquinolines. Snyder, Cohen and Tapp (4,5) condensed dimethylacetylenedicarboxylate with cinnamalaniline to obtain two isomeric addition products. The lower melting isomer was studied by Snyder, Tapp, Anderson, Neville and Shelberg (5,6,7,8,9). On the basis of the evidence obtained, Shelberg postulated the structure to be 1-phenylamino-2-benzal-3,4,5,6-tetracarbomethoxy-1,2-dihydrobenzene. The present study was made in an effort to determine with certainty the structure of this condensaion product.

DISCUSSION

Ozonolysis of the condensation product and reductive decomposition of the ozonide yielded benzaldehyde, but no other product could be isolated. No isomerization took place when the adduct was refluxed in solution with palladium (10%) on charcoal. In an attempt at thermal degradation, a methanol solution of the dihydro derivative of the original material was heated in an autoclave at 270°C. for a half an hour. The dihydro compound was also heated dry at 300°C. for two minutes. Both experiments produced only tar.

A monobasic acid was obtained through saponification of the condensation product, but no pure material could be isolated in which more than one ester group had been saponified. In an attempt to prepare the tetracarboxylic acid by synthesis, dimethylacetylenedicarboxylic acid was added to a dioxane solution of cinnamalaniline. The only product isolated was salt of the anil.

Infra-red analysis of the condensation product indicated that no secondary amine group was present.

When a solution of the condensation product in a mixture of acetic acid and hydrobromic acid was heated under

reflux for five hours, a white, crystalline product was obtained. Analysis showed it to have the empirical formula $C_{13}H_9O_5N \cdot H_2O$. The material had no ester groups and was a dibasic acid. Heating this product to its melting point caused the evolution of carbon dioxide, but no crystalline material could be isolated from the residue. Ultra-violet and infra-red spectra indicated that both the ring structure and carbonyl group present were similar to those of N-methylpyridone.

On the basis of this evidence, the acid cleavage product was postulated to be an N-phenyl-2-pyridonedicarboxylic acid, and the original condensation product is believed to be N-phenyl-2-(β-styryl)-3,4,5,6-tetracarbomethoxy-1,2-dihydropyridine.

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VITA

The author was born in Chicago, Illinois, on May 14, 1919. He attended Longfellow grammar school in Oak Park, Illinois, and graduated from Oak Park and River Forest Township High School in 1936. He attended Augustana College in the fall of the same year and graduated with an A.B. degree in June, 1940. In September, 1940, he enrolled in the Graduate School of the University of Illinois and held a teaching assistantship from that time until July 1, 1943. From September, 1943, until May, 1944, he was employed by the University on a research assistantship and held that position again from October, 1945, until September, 1946. During the period from May, 1944, until September, 1945, he was employed as a junior chemist by Tennessee Eastman Corporation, Oak Ridge, Tennessee.

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